

REMARKS**Claim Amendments**

Claim 25 has been amended to recite that the polyazole polymer formed has an intrinsic viscosity of at least 1.4 dl/g. Support for this amendment can be found, for example, on page 15, lines 7-10 and page 20, lines 36-39 of the Specification and in Claims 47 and 48 of the application.

Claim 47 has been cancelled.

Claim 48 has been amended to more clearly define that which Applicants regard as the invention. Support for this amendment can be found, for example, on page 15, lines 7-10 and page 20, lines 36-39 of the Specification and in Claims 47 and 48 of the application.

Rejection of Claim 25 and claims dependent thereon under 35 U.S.C. §102(e)

Claim 25 and claims dependent thereon are rejected under 35 U.S.C. §102(e) as being anticipated by WO 02/071518 (“‘518”).

The Examiner stated that applied reference has common inventors with the instant application. Furthermore, the Examiner stated that based upon the earlier effective US filing date of the reference, it constitutes prior art under 35 U.S.C. §102(e).

Applicants respectfully disagree with the Examiner’s statement. Applicants note that the ‘518 International application was published in German, on September 12, 2002, therefore it is available under U.S. law as a prior art only as of its publication date. Instant Application claims priority to the German Application 102 39 701.5, filed on August 29, 2002. Since publication date of ‘518 is subsequent to the earliest priority date of the instant application, the ‘518 does not constitute prior art under 35 U.S.C. §102(e) or 35 U.S.C. §102(a).

In the view of the above, Claim 25 is novel over ‘518. Claims 26-46 and 48-51 depend directly or indirectly on independent Claim 25 and, therefore, are also novel.

Reconsideration and withdrawal of the rejection are respectfully requested.

Rejection of Claim 25 and claims dependent thereon under 35 U.S.C. §102(a) and §102 (e)

Claim 25 and claims dependent thereon are rejected under 35 U.S.C. §102(a) and §102(e) as being anticipated by WO 02/36249 (“‘249”). Specifically, the Examiner stated that ‘249 discloses a single-layered or multi-layered plastic membrane doped with acid. The layer disclosed in ‘249 is comprised of a polyazole disclosed in the instant application (‘249, formula 1C at page 6 and Claim 3 at page 19).

The membrane disclosed in ‘249 is different than the product produced by the claimed process of the instant application. The ‘249 membrane is doped with acid, and the presence of the acid in the membrane is important for the improved mechanical and physicochemical properties of the membrane, for example, good proton conductivity (see Exhibit A, U.S. Application Number 10/399,514, the U.S. National Stage Application of the ‘249 Application, page 1, paragraph 8). Exhibit A further states that that “the doped polymer membranes are polymer membranes which due to the presence of dopants display an increased proton conductivity compared to the undoped polymer membranes” (page 4, paragraph 45). Furthermore, Exhibit A teaches that increasing the degree of doping increases the conductivity of the material, and consequently, a doping of 6-12 mole of acid per mole of repeat unit is preferred (page 4, paragraph 47 and Table 1). Exhibit A further states that the preferred dopant is phosphoric acid (page 4, paragraph 46).

In contrast to ‘249, the instant invention provides a new class of polymer films based on polyazoles. Specifically, amended Claim 25 requires “removing the polyphosphoric acid or phosphoric acid present and drying” (see Step F). Completion of Step F of the claimed process results in a film that is different from the film of ‘249 because Step F removes the phosphoric acid that corresponds to the dopant of ‘249. As a result, the undoped film of the instant invention has a porous structure that is morphologically different to that of the film disclosed in ‘249, in which the film is doped with acid (instant application, page 19, lines 6-7).

For the above reason alone, amended Claim 25 is novel in view of ‘249. Furthermore, Claim 25 has been amended to recite that the polyazole polymer formed has an intrinsic viscosity of at least 1.4 dl/g. ‘249 does not teach the intrinsic viscosity of the polymeric films formed therein. Therefore, amended Claim 25 is novel in view of ‘249.

Amended Claim 25 is also non-obvious in view of '249 because the instant application selects a polyazole polymer with an intrinsic viscosity of at least 1.4 dl/g, which corresponds to the selection of a high molecular weight polyazole polymer. These high molecular weight polyazoles of the instant application have unexpected advantages in mechanical properties and are, therefore, non-obvious in view of '249.

Intrinsic viscosity is defined by IUPAC as:

intrinsic viscosity (of a polymer)

The limiting value of the *reduced viscosity*, η_i/c , or the *inherent viscosity*, η_{inh} , at infinite dilution of the polymer, i.e.

$$[\eta] = \lim_{c \rightarrow 0} (\eta_i/c) = \lim_{c \rightarrow 0} \eta_{inh}$$

Here, c is the concentration of a polymer, and η_i is the *relative viscosity increment*, defined by IUPAC as the ratio of the difference between the viscosities of solution and solvent to the viscosity of the solvent. See URLs <http://www.iupac.org/goldbook/I03140.pdf> (submitted herewith as Exhibit B) and <http://goldbook.iupac.org/R05283.html> (submitted as Exhibit C), both last accessed on December 2, 2008.

Intrinsic viscosity is related to molecular weight by the Mark-Houwink equation. (See Exhibit D, J. Brandrup and E.H. Immergut, *Polymer Handbook*, 3rd Ed., Wiley Interscience (1989), pp. VII/1, and Exhibit E, a Guide on Determination of Molecular Weight, downloaded from the website run by the University of California College of Engineering, at URL <http://www.eng.uc.edu/~gbeaucag/Classes/Characterization/MolecularWeight.html/MolecularWeight.html> (last accessed December 2, 2008).) As can be seen from the Mark-Houwink equation, intrinsic viscosity η is directly proportional to the molecular weight M . (See Exhibit D.) Thus, the higher the intrinsic viscosity of a solution of a solute, the higher the molecular weight of the solute that is dissolved in the solution.

Selection of materials with high molecular weight (as evidenced by higher intrinsic viscosity) results in unexpected improvements of the mechanical properties of the claimed polymer film of the instant application. For example, advantages of the high molecular weight claimed process polymer films of the invention include long-term stability and product life, and improved separation behavior (page 18, lines 29-31). Additionally, the claimed polymer film do not contain impurities which require high cost to remove (page 18, line 32-33).

In the view of the above, Claim 25, as amended, is novel over '249 because the polymer films of '249 are doped with a dopant, such as phosphoric acid, and therefore different than the undoped porous polymeric film of the claimed invention. Additionally, '249 does not teach the selection of high molecular weight materials, and consequently, Claim 25, as amended, is novel in view of '249. Furthermore, the high molecular weight polymer films of amended Claim 25 have unexpected improved mechanical properties. Therefore, amended Claim 25 is non-obvious over the teachings of '249. Claims 26-46 and 48-51 depend directly or indirectly on independent Claim 25 and, therefore, are also novel and non-obvious.

Reconsideration and withdrawal of the rejection are respectfully requested.

Rejection of Claim 25 and claims dependent thereon under 35 U.S.C. §102(b)

Claims 25 and claims dependent thereon are rejected under 35 U.S.C. §102(b) as being anticipated by EP 0265921 ("921"). Specifically, the Examiner stated that the '921 reference discloses an organic optical component comprising a medium of polybenzimidazole, which is a polyazole disclosed in the instant application (page 3, last formula, page 7, Example II and Claim 8).

The membrane disclosed in '921 is different than the membrane produced by the claimed process of the instant application. '921 discloses optical devices with an organic non-linear optical film. '921 discloses in Example II that the preparation of polybenzimidazole (PBI) polymers is done using two-stage solid polymerization process (on page 7, lines 26-57). The resulting PBI has a *low* molecular weight (reported as inherent (intrinsic) viscosity of 0.95dl/g, when prepared with a catalyst (page 7, line 51) or 0.56 dl/g, when prepared without a catalyst (7, line 56)).

In contrast to '921, the instant invention provides a new class of polymer films based on polyazoles. Claim 25 has been amended to recite that the polyazole polymer formed has an intrinsic viscosity of at least 1.4 dl/g. The intrinsic viscosity of the polymer films disclosed in '921 are lower (*e.g.* 0.56- 0.95 dl/g) than the polymeric films formed from the claimed process. Therefore, the polymer films of '921 are different than the polymer films of the instant application. Moreover, '921 does not teach removal of acid to generate membrane films that possess a porous morphology. Instead, '921 teaches heating the material to form the polymer,

but does not mention removing any acid present to produce a membrane with a porous structure as the instant application does in Step F if amended Claim 25.

For the reasons above, amended Claim 25 is novel in view of '921.

Amended Claim 25 is also non-obvious in view of '921 because the materials claimed in Claim 25 of the instant application are a selection of a polyazole polymer with an intrinsic viscosity of at least 1.4 dl/g, which corresponds to the selection of a high molecular weight polyazole polymer. These high molecular weight polyazoles of the instant application have unexpected advantages in mechanical properties and are, therefore, non-obvious in view of '921.

As discussed above, the high intrinsic viscosity, which corresponds to a high molecular weight, of the polyazole polymer formed from the claimed process results in unexpected improvements of the mechanical properties of the claimed polymer film. For example, advantages of the high molecular weight polymer films of the invention include long-term stability and product life, and improved separation behavior (page 18, lines 29-31). Additionally, the claimed polymer film do not contain impurities which require high cost to remove (page 18, line 32-33).

In the view of the above, Claim 25, as amended, is novel over '921 because the polymer film of '921 are of a lower molecular weight and are not treated to remove any acid present to produce a membrane with a porous morphology, and therefore are different than the claimed polymer films. Additionally, the high molecular weight polymer films of amended Claim 25 have unexpected improved mechanical properties. Therefore, amended Claim 25 is non-obvious over the teachings of '921. Claims 26-46 and 48-51 depend directly or indirectly on independent Claim 25 and, therefore, are also novel and non-obvious.

Reconsideration and withdrawal of the rejection are respectfully requested.

CONCLUSION

In view of the above amendments and remarks, it is believed that all claims are in condition for allowance, and it is respectfully requested that the application be passed to issue. If the Examiner feels that a telephone conference would expedite prosecution of this case, the Examiner is invited to call the undersigned.

Respectfully submitted,

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Date: 12/3/08

intrinsic viscosity (of a polymer)

The limiting value of the *reduced viscosity*, η_i/c , or the *inherent viscosity*, η_{inh} , at infinite dilution of the polymer, i.e.

$$[\eta] = \lim_{c \rightarrow 0} (\eta_i/c) = \lim_{c \rightarrow 0} \eta_{inh}$$

Notes:

1. This term is also known in the literature as the Staudinger index.
 2. The unit must be specified; $\text{cm}^3 \text{g}^{-1}$ is recommended.
 3. This quantity is neither a viscosity nor a pure number. The term is to be looked on as a traditional name. Any replacement by consistent terminology would produce unnecessary confusion in the polymer literature.
- Synonymous with limiting viscosity number.

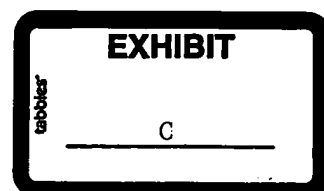
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relative viscosity increment

The ratio of the difference between the viscosities of solution and solvent to the **viscosity** of the solvent, i.e. $\eta_i = \frac{(\eta - \eta_s)}{\eta_s}$, where η is the **viscosity** of the solution and η_s is the **viscosity** of the solvent. The use of the term 'specific **viscosity**' for this quantity is discouraged, since the **relative viscosity** increment does not have the attributes of a specific quantity.

Source:

Purple Book, p. 63



POLYMER HANDBOOK

THIRD EDITION

Edited by

J. BRANDRUP and E. H. IMMERGUT

F+E GB-Z, 832 (Zentr. Polymer Forsch.)

Hoechst Aktiengesellschaft FRANKFURT (M) - HÖCHST	
18. III. 1993 * 1419	
Doc:	108017
Cap:	179180

Z 37/5



A WILEY-INTERSCIENCE PUBLICATION

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New York • Chichester • Brisbane • Toronto • Singapore

EXHIBIT

D

Viscosity-Molecular Weight Relationships and Unperturbed Dimensions of Linear Chain Molecules

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A. INTRODUCTION

1. The Viscosity-Molecular Weight Relationship

The limiting viscosity number $[\eta]$ of a solution which has long been called the intrinsic viscosity is defined as

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta - \eta_0}{\eta_0 c} \quad (1)$$

in terms of the solvent viscosity η_0 , the solution viscosity η , and

the solute concentration c . The concentration c is expressed in grams of solute per milliliter of solution or, more frequently, in grams of solute per 100 milliliters of solution, the limiting viscosity number being given in the reciprocal of these units, i.e., in milliliters per gram or in deciliters per gram. Here, following the IUPAC 1952-recommendations (1), we adopt the former unit. The quantity $[\eta]$ of a polymer solution is a measure of the capacity of a polymer molecule to enhance the viscosity, which depends on the size and the shape of the polymer molecule. Within a given series of polymer homologs, $[\eta]$ increases with the molecular weight M ; hence it is a measure of M .

Table C gives the limiting viscosity number—molecular weight relationships for polymers in various solvents and at various temperatures. The table contains the constants of the equation

$$[\eta] = KM^a \quad (2)$$

which is known as the Mark-Houwink-Sakurada equation.

It is now well established that for linear, flexible polymers, under special condition of temperature or solvent, (usually known as the Flory 'theta' temperature or solvent (2)), the above equation becomes

$$[\eta]_\theta = K_\theta M^{0.50} \quad (3)$$

The sign θ in front of the temperature data in the table indicates that the viscosity constants were obtained under the θ condition. Since Eq. (3) is approximately valid over the whole molecular weight range, K_θ and $a = 0.50$ may be used, without modification outside of the molecular weight range in which they were determined. However, it must be noted that $[\eta]$ is rather sensitive to temperature in the vicinity of θ , especially when M is higher than 5×10^5 .

In ordinary good solvents, the constants K and a obtained are valid only within a rather limited range of M (3,4). It is, therefore, quite probable that the tabulated relationships are in error outside the indicated range of M (see eighth column in the table). As for the effect of temperature, however, both K and a mostly become insensitive to the temperature when a exceeds about 0.70, and they may be used in a ten-degree range on either side of temperature at which the constants were determined.

The method of determination of the molecular weight and the number of fractionated samples (Fr.) or whole polymer samples (W.P.) used to determine the $[\eta]$ - M relationship are also given in the ninth and the sixth or seventh columns, respectively. The abbreviations used are as follows:

(A) Methods Yielding the Number-Average Molecular Weight, M_n
 CR, cryoscopy
 EG, end-group titration
 VOS, vapor pressure osmometry
 EB, ebullioscopy
 OS, osmotic pressure

(B) Methods Yielding the Weight-Average Molecular Weight, M_w
 LS, light scattering
 SE, sedimentation equilibrium
 SA, approach to the sedimentation equilibrium (Archibald's method)

(C) Empirical or Semi-Empirical Methods

EM, electron microscopy
 GPC, gel permeation chromatography
 LV, limiting viscosity number—molecular weight relationship
 PR, analysis of polymerization rate (yielding M_n)
 DV, diffusion and viscosity
 MV, melt viscosity—molecular weight relationship
 SD, sedimentation and diffusion
 SV, sedimentation and viscosity

Thus, for example, the constants tabulated are for the $[\eta]$ - M relationships expressed in terms of M_n or M_w if the method is specified as OS or LS, respectively; i.e.,

$$[\eta] = K_n M_n^a \quad (4)$$

or

$$[\eta] = K_w M_w^a \quad (5)$$

The values of K_n and K_w , especially the former, are greatly influenced by the molecular weight distribution (MWD) of the polymer samples, and caution must be taken in using these relationships.

To illustrate this effect, let us assume that:

(i) Eq. (2) is applicable to the molecule i with molecular weight M_i over the whole range of M ; i.e.,

$$[\eta]_i = K M_i^a \quad (6)$$

(ii) The weight fraction w_i of the molecules i in a given sample can be represented by a continuous exponential function,

$$w_i(M_i) = [y^{h+1}/\Gamma(h+1)] M_i^h \exp(-yM_i) \quad (7)$$

$$y = h/M_n = (h+1)/M_w \quad (8)$$

or by the log-normal function,

$$w_i(M_i) = AM_i \exp[-p^2(\ln M_i/M_0)^2] \quad (9)$$

where h , A , p , and M_0 are constants, and Γ represents the gamma function.

Then, since $[\eta] = \sum_i w_i [\eta]_i$, we obtain

$$K_n = K\Gamma(a+h+1)/h^a\Gamma(h+1) \quad (10)$$

$$K_w = K\Gamma(a+h+1)/(h+1)^a\Gamma(h+1) \quad (11)$$

for the exponential MWD, and

$$K_n = K(M_w/M_n)^{0.5a(a+1)} \quad (12)$$

$$K_w = K(M_w/M_n)^{0.5a(a-1)} \quad (13)$$

for the log-normal MWD (5). The values of K_n/K and K_w/K calculated by these equations are shown in Table B. This table may be used for estimating an error due to MWD in determination of M .

As an example, let us assume that a given polymer sample has the exponential MWD with $M_w/M_n = 2.0$, while an available $[\eta] - M_n$ equation has been obtained for samples with a narrow

MWD, e.g., $M_w/M_n = 1.1$. Further, let a be 0.70. Then, to find the correct value of M_n of the given sample from $[\eta]$, we must use the equation (4) with $K_n = 1.54K$, instead of the available equation with $K_n = 1.06K$. Use of the latter would lead to an overestimate M'_n which is related to the correct M_n by

$$[\eta] = 1.54K M_n^{0.70} = 1.06K M'_n{}^{0.70} \quad (14)$$

The error amounts to about 70%, i.e., $M'_n = 1.7M_n$. Thus, application of the viscosity equation written in M_n is to be restricted to within a narrow class of samples, unless an appropriate correction is made. On the other hand, if an $[\eta]-M_w$ equation is available for the same pair of working and reference samples as above, we have

$$[\eta] = 0.951K M_w^{0.70} = 0.991K M'_w{}^{0.70} \quad (15)$$

instead of Eq. (14). Hence, the error M_w amounts to only 6% ($M'_w = 0.94M_w$), which will be negligible for more practical purposes.

Based on the above consideration, we classify the heterogeneity of polymers in four classes, A to D, as shown in the last column of Table B, and indicate it in the tenth column of Table C as a measure of the heterogeneity of the reference samples used.

It is desirable that readers select their own relationship by inspecting these data on heterogeneity as well as those on the number of samples and molecular weight range. Generally speaking, a 'good' $[\eta]-M$ relationship is one that has been obtained on the basis of M_w for at least four samples of classes A and B (exceptionally C) or on the basis of M_n for those of class A (exceptionally B), whose molecular weights range over at least one half orders of magnitude.

In the 'Remarks' column of Table C, we have occasionally indicated by the letter R a 'recommended' relationship for the convenience of readers. In the range of low molecular weight (mostly less than 10^4), the constant a becomes 0.50 irrespective of solvent. This type of relationship can not be used, even approximately, at higher molecular weights. This case is noted by the letter L. High conversion polymers are also marked by the letter H, where the $[\eta]-M$ relationships are less reproducible due to chain branching than are ordinary ones. The abbreviations used are as follows.

- A narrow MWD polymers, or well-fractionated polymers, $M_w/M_n \leq 1.25$
- B ordinary fractionated polymers, $1.30 \leq M_w/M_n \leq 1.75$
- C poorly fractionated polymers or most probable MWD polymers, $1.8 \leq M_w/M_n \leq 2.4$
- D wide MWD polymers, $M_w/M_n \geq 2.5$
- H high conversion polymers, including branches
- L limited to low-molecular-weight polymers
- R recommended relationship

In this table, polymers are arranged according to their structure in subgroups. Within each subgroup, the polymers are, in principle, given in alphabetical order. Within each polymer, the solvents are also arranged in alphabetical order, followed by the mixed solvents.

Chain configurational data are occasionally given in the first column. The data given in parentheses refer to only one set of viscosity constants listed in the same row, while the data given

without parentheses refer to a series of sets listed in the same and succeeding rows. Thus, for example, the data 'N content, 13.9 wt%' are effective only for the sixth row of cellulose trinitrate, and the data '95%-cis, 1%-trans, 4%-1,2' are effective for the fourth to eighth rows of polybutadiene.

Table C is essentially based on the table published by Kurata and Stockmayer (3). Data were also taken from tables published by Peterlin (7), Meyerhoff (8), Elias (9), and Krause (10), the last one including a number of unpublished data on acrylic and methacrylic polymers. We are also grateful to these authors. Thanks are tendered also to J. Brandrup and K. Kamide for their help with this compilation.

2. Unperturbed Dimensions of Linear Chain Molecules

The mean-square end-to-end distance $\langle r^2 \rangle$ of a linear chain molecule in solution is usually expressed in terms of two basic quantities, the unperturbed mean-square end-to-end distance $\langle r^2 \rangle_0$ and the expansion factor α ; i.e.,

$$\langle r^2 \rangle = \langle r^2 \rangle_0 \alpha^2 \quad (16)$$

The latter quantity α represents the effect of 'long-range interactions' which can be described as an osmotic swelling of the chain by the solvent-polymer interactions, while the unperturbed dimension $\langle r^2 \rangle_0$ represents the effect of 'short-range interactions' such as bond angle restrictions and steric hindrances to internal rotation. The steric hindrances are also influenced by the torques exerted on the chain by solvent molecules, but the effect is rather small in many cases (11).

For sufficiently long chain, $\langle r^2 \rangle_0$ becomes proportional to $\sum_i n_i l_i^2$, where n_i is the number of the i th-kind bond of length l_i . The quantity C_∞ defined by

$$C_\infty = \lim_{n \rightarrow \infty} \langle r^2 \rangle_0 / \sum_i n_i l_i^2 \quad (17)$$

is often called the characteristic ratio and it serves as a measure of the effect of short-range interactions.

The freely rotating state is a hypothetical state of the chain in which the bond angle restrictions are retained, but the steric hindrances to internal rotation are released. The mean-square end-to-end distance of the freely rotating chain $\langle r^2 \rangle_{or}$ can be readily calculated from the given basic structure of the chain. For instance, if the chain consists of only one kind of bond of length l , we obtain

$$\langle r^2 \rangle_{or} = nl^2 [(1 + \cos \theta)/(1 - \cos \theta)] \quad (18)$$

where n is the number of bonds and θ is the supplement of the valence bond angle. For vinyl polymer chains, $l = 0.154$ [nm], $\cos \theta = 1/3$, and $n = M/m = 2M/M_u$; and hence

$$(\langle r^2 \rangle_{or}/M)^{1/2} = 0.308/M_u^{1/2} = 0.218/m^{1/2} \text{ [nm]} \quad (19)$$

where M_u is the molecular weight of the repeating unit and m is the average molecular weight per skeletal link. Similar expressions for $r_{or} (= \langle r^2 \rangle_{or}^{1/2})$ can be obtained also for more complicated chains. The results are summarized in Table D.

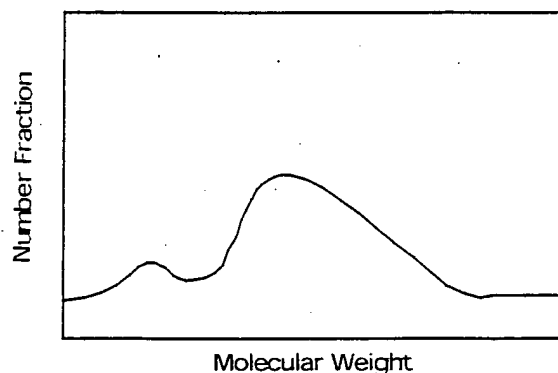
The ratio of $\langle r^2 \rangle_0$ to $\langle r^2 \rangle_{or}$, then, represents the effect of steric hindrance on the average chain dimension:

$$\sigma = r_0/r_{or} = (\langle r^2 \rangle_0 / \langle r^2 \rangle_{or})^{1/2} \quad (20)$$

The quantity σ is independent of n . Table E gives a list of the unperturbed dimensions of linear chain molecules which were

Determination of Molecular Weight

The distinguishing feature of commercial polymers is that they have molecular weights far in excess of the entanglement molecular weight of about 10,000 g/mole. From typical industrial synthesis a fairly broad distribution in molecular weight results. The features of this distribution have dramatic effects on the processability (viscosity) and properties (miscibility, strength and modulus) of plastics. Consider a plot of the fraction of a plastic sample with a specified molecular weight versus molecular weight as show below.



The distribution shown above is **bimodal** (two identifiable peaks) and skewed (neither of the peaks is a symmetric about their means and the entire bimodal distribution is not symmetric about the mean. Such a distribution of molecular weights can be described by statistics in terms of moments.

The simplest description of a unimodal (one peak) symmetric distribution (same on both sides of the peak) will involve two parameters, the **mean**, μ and the **standard deviation**, σ . More complicated continuous distribution functions will involve higher moments of the distribution. The k'th moment of a distribution about a value, x_s , is given by:

$$k\text{'th moment} = \sum_i f_i (x_i - x_s)^k$$

where f_i is the fraction of all measurements which have the value x_i , i.e. N_i/N , x_s is basis for the moment and k is the order of the moment. For example, the mean, μ , is the first moment ($k = 1$) about the origin ($x_s = 0$). The variance, σ^2 , is the second moment ($k = 2$) about the mean ($x_s = \mu$).

In polymer science it is the convention to define several special parameters to describe molecular weight distributions. The number average, weight average, z-average and viscosity average. These parameters can be described in terms of the more broadly used statistical description of moments given above.

The **number average molecular weight**, M_n is the same as **the first moment about the origin** or the **mean**. The weight average molecular weight (mass average), M_w , is given by:

$$M_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} = \frac{\sum_i f_i M_i^2}{\sum_i f_i M_i}$$

EXHIBIT

E

or the **ratio of the second to the first moment about the origin**.

The polydispersity index, M_w/M_n , is the ratio of the second moment to the square of the first moment about the origin.

Given M_w and M_n the standard deviation of a distribution of molecular weights can be determined:

$$\sigma = M_n \left(\frac{M_w}{M_n} - 1 \right)^{1/2}$$

The **z-average** is the **third moment about the mean divided by the second moment about the mean**.

For a simple unimodal symmetric distribution only the first and second moments are needed to describe the distribution if a functional form such as a Gaussian or Lorentzian distribution is appropriate. For skewed distributions the third moment and perhaps higher order moments are needed such as in the Maxwellian distribution. In general, the number of distinct moments needed to fully describe a distribution is equal to the number of features in the distribution curve. For instance the distribution shown above would require at least two moments to describe the first peak (assuming it is symmetric and could be generated using a Gaussian function), at least three moments to describe the second peak (assuming it can be described by a Maxwellian distribution) and a sixth parameter which relatively weighted the two peaks of the bimodal distribution. Such a bimodal distribution could not be fully describe by just M_w and M_n for instance.

Methods for Characterization of Molecular Weight

Analytic techniques for the determination of molecular weight can be broken down into **primary** and **secondary techniques** based on whether or not standards are needed to calibrate the analytic instrument.

Many primary or **absolute** techniques are based on colligative properties of the polymer such as melting point depression, vapor pressure and osmotic pressure. Other primary techniques use scattering and chemical analysis of end groups. None of the primary techniques are used on a routine basis as they all involve a significant effort and generally yield only one moment of molecular weight. Intrinsic viscosity is theoretically a primary technique, in that for the theta solvation conditions secondary standards are not necessary. In usual practice, at non-theta conditions, intrinsic viscosity relies on knowledge of the Mark-Houwink coefficients for the thermal and solvent conditions of measurement.

An absolute determination of molecular weight for a single sample using light scattering, for example, might take the better part of a week including sample preparation, filtration, running the experiment and preparation of Zimm plots. Use of a solution light scattering instrument usually requires prior experience and can be frustrating in that unknown sources of dust in the sample can often corrupt the data.

The most commonly used techniques are **relative techniques** since sample preparation and the actual measurement are much simpler and more reproducible. Of secondary techniques, gel permeation chromatography (GPC) (also known as high pressure liquid chromatography, HPLC) is the most versatile and useful technique. GPC results in measurement of the entire molecular weight distribution (see figure above) from which any of the moments of molecular weight or common polydispersity indices can be calculated. For a new polymer a GPC is usually calibrated using monodisperse standards, most commonly polystyrene standards, which are available from

most chemical suppliers such as Aldrich, Polymer Labs, and Pressure Chemicals. The molecular weight is then given in terms of the equivalent polystyrene molecular weight and must be so noted. Rarely, it is necessary to develop a new set of standards for an unknown sample, most commonly using light scattering. Training for use of a GPC is rapid and useful results are obtained, usually in the first attempt. Sample preparation and measurement of a molecular weight distribution using GPC requires about 1 day.

In the characterization lab two techniques for determination of molecular weight are introduced, intrinsic viscosity and use of the GPC. Intrinsic viscosity measurement is typical of an absolute technique and the purpose of this lab is to introduce the problems which are common to such techniques. Measurement of the intrinsic viscosity can be a frustrating and messy enterprise.

Intrinsic Viscosity:

The Polymer Handbook (3rd edition Brandrup and Immergut) lists values for the Mark-Houwink equation as well as a concise description of the intrinsic viscosity (by Kurata and Tsunashima) in section VII. Some of this description is summarized below.

Consider a polymer in solution at low concentrations $<1\%$. The polymer, typically, takes a self-avoiding walk conformation, $R \propto n^{3/5}$, associated with good solvent conditions (n is the molecular weight and R is a measure of the polymer size, here the most probable size). If the temperature is lowered to just above the temperature of phase separation, the coil size is reduced and at some point in this decline in size the theta condition is met where the coil follows Gaussian statistics, $R \propto n^{1/2}$. A theoretical description of this behavior is given in Polymer Physics Notes Chapters 1 and 2.

A second way to obtain Gaussian scaling is to increase the concentration of the solution. As concentration is increased the coils will begin to overlap. The overlap concentration, c^* , can be calculated if an estimate of the coil size is available. For high-concentrations ($>40\%$) and in the melt the presence of a large number of interpenetrating chains leads to screening of the interactions which lead to solvation of the chains. The chains are subjected to a mean-field which means that the interactions between chains and solvent are smeared. Under these conditions the coil can be shown to display Gaussian statistics.

The intermediate regime between dilute and concentrated conditions are not well understood, but have been partially explained in terms of a special kind of statistical transition in behavior between good solvent and Gaussian behavior. The mathematical tool which allows for a description of this transition is called renormalization. Renormalization is one of the major success stories of polymer physics in the past 20 years.

For the purpose of measurement of intrinsic viscosity all of this is of minor importance. The main consequence is that measurements of molecular weight must involve dilute conditions so as to avoid the overlap concentration and complications which basically can not be resolved. The viscosity of such a dilute solution depends on the viscosity of the solvent, η_0 , and an effect related to the presence of isolated polymer coils in the solution. There is solvent entrapped in a single, isolated coil, but this solvent does not directly contribute to the viscosity since it is shielded from shear flows in the solution by the polymer coil. This is called the non-draining hypothesis and is a basis of intrinsic viscosity measurements. If the solvent in the coil is entrapped, then the isolated polymer coil is from the perspective of a dynamic experiment (here rheology or fluid flow) a sphere whose size depends on the solvation condition of the coil and short range interactions which effect the persistence length of the chain. Stokes law and the Einstein equation tells us that the enhancement of viscosity due to the presence of these "spheres" can be simply described by the

first two terms of a power series expansion, $\eta = \eta_0 (1 + k \phi)$, where k is a constant defined by for spheres as 2.5, and ϕ is the volume fraction of spheres. The use of only the first two terms is justified as the equation is only appropriate at low concentrations so $\phi^2 \ll \phi$. The mass per unit volume, c_2 , is related to the volume fraction, ϕ , by $\phi = c_2 V_{\text{molar}}/M$, where M is the molecular weight and V_{molar} is the partial molar volume of the polymer in solution.

The **intrinsic viscosity** is obtained in the limit of $c_2 \rightarrow 0$ as $[\eta] = (\eta - \eta_0)/(c_2 \eta_0)$. From the Einstein equation, it is clear that $[\eta] = 2.5 \phi / c_2 = 2.5 V_{\text{molar}}/M$. M/V_{molar} is essentially the density of the coil, i.e. the coil mass divided by the coil volume. The units of intrinsic viscosity are inverse concentration. Under theta conditions, $R \propto M^{1/2}$ and $V \propto R^3 \propto M^{3/2}$, so $[\eta] = K M^{1/2}$. The constant K depends on primary molecular features such as the persistence length, so for a Gaussian coil can be calculated from first principles.

The determination of the intrinsic viscosity involves a flow experiment, so that the volume and radius involved are not really the end-to-end distance for the coil or the most probably size. A new measure of size, the hydrodynamic radius, R_H , and hydrodynamic volume, V_H , are needed. These new parameters are assumed to have the same molecular weight dependence as the end-to-end distance and radius of gyration for the coils. The hydrodynamic parameters are essentially empirical, i.e. these are measured and not really fundamental quantities. There is some literature available on a theoretical basis for hydrodynamic measures of size in the colloid literature, much of it based on the work of Simha at Case Western.

Generally, the intrinsic viscosity is measured under non-theta conditions so an empirical equation is used to describe the intrinsic viscosity/molecular weight relationship, the Mark-Houwink equation, $[\eta] = K M^a$, where a and K are constants for a specific polymer/solvent/temperature system. At the theta condition a should go to 1/2. For non-theta conditions $a > 1/2$. For good-solvent scaling a is expected to be 3/5. " a " varies from the values of 1/2 or 3/5 due to short-range interactions and their implied effect on the definition of M . Branched polymers can have a value of a less than 1/2. Values greater than 0.6 are usually associated with chain rigidity and asymmetry of the coil due to features such as helical coiling.

The viscometer used to measure dilute solution viscosity is usually a capillary viscometer. This viscometer uses the Poiseuille equation for laminar pressure flow in a capillary tube. The volumetric flow rate, $Q = \Delta V / \Delta t$, under gravity, following Poiseuille's law is given by, $Q = \rho g \pi R^4 / (8 \eta)$. For constant volume, ΔV , the time for flow is proportional to the viscosity, $t = k \eta$. (Poiseuille's law for pressure and gravity driven flow is $Q = (\rho g H + \Delta p) \pi R^4 / (8 \eta H)$.)

Since time is proportional to viscosity, the intrinsic viscosity can be calculated from a capillary viscometer substituting time for viscosity, the limit of $c_2 \rightarrow 0$ as $[\eta] = (t - t_0) / (c_2 t_0)$.

GPC:

Gel permeation chromatography involves passing a dilute polymer solution through a tubular column packed with polymeric gel (crosslinked) beads. Under high pressure flow some of the polymer chains are forced into the pores of the gel, while others pass by the gel beads. The residence time of a given polymer chain in the packed column depends on the path it takes through the gel. For instance, a low molecular weight oligomer will easily be forced into the pores of the gel and will take a circuitous path through the column, traveling a distance equivalent to hundreds of the column length. High molecular weight species can not fit into the pores of the gel, i.e. they are

excluded, and can pass more directly to the exit of the column traveling a distance roughly equivalent to the column length. The selectivity of this process for molecular weight is outstanding and the range of molecular weights which can potentially be characterized by this technique is only limited by the ability to produce controlled spaced gels. GPC is by far the most versatile technique for the determination of molecular weight in a polymer sample.

GPC is called different names in different fields. Organic chemists call it size exclusion chromatography (SEC), high-pressure liquid chromatography (HPLC), gel filtration chromatography (GFC) and variants of these such as HPSEC, HPGFC, HPGPC. There may be some minor differences but the instruments are basically all the same thing.

In GPC a sample of polymer in dilute solution is injected into the chromatograph at an instant of time, t_0 . The chromatographic column and pumps are pumping the same solvent, albeit with no polymer. A detector is used to note the overall concentration of polymer in the eluted solvent (solvent which has passed through the column) as a function of time at constant volumetric flow rate, Q . The time at constant flow rate reflects a volume of fluid which has eluted from the column, i.e. the elution volume. The time it takes the polymer to elute from the column is called the retention time, t_R , and the elution volume for this time is called the retention volume, V_R . If the right gel is inserted in the column for the molecular weight range of interest, the relation between V_R and molecular weight is linear, $V_R = V_{R0} - kM$, where M is the molecular weight, k and V_{R0} are constants for a particular polymer/solvent/gel system. The two constants are determined by eluting two or more monodisperse standards. If monodisperse standards are not available, a reference polymer such as polystyrene is used and the molecular weight is given in terms of a polystyrene equivalent molecular weight.

The detector in a GPC must be linear with concentration. Typically a refractometer, for measurement of index of refraction is used. Many other detectors can be used in a GPC and much of the recent development in liquid chromatography has focused on the use of different detectors such as spectrometers, viscometers and light scattering detectors.

The output of a GPC is considered to reflect the number of chains at a given retention volume or molecular weight. From a GPC curve all of the molecular weight distributions, noted above, can be determined. The GPC is the only simple technique to determine the modality (bimodal, trimodal etc.) of a polymer sample.



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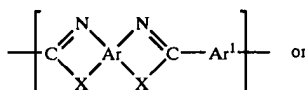
(19) **United States**(12) **Patent Application Publication**
Soczka-Guth et al.(10) **Pub. No.: US 2004/0131909 A1**(43) **Pub. Date: Jul. 8, 2004**(54) **NOVEL MEMBRANES HAVING IMPROVED
MECHANICAL PROPERTIES, FOR USE IN
FUEL CELLS**(76) **Inventors: Thomas Soczka-Guth, Schelklingen
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Frauke Jordt, Eppstein (DE)****Correspondence Address:**
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WILMINGTON, DE 19899 (US)(21) **Appl. No.: 10/399,514**(22) **PCT Filed: Oct. 20, 2001**(86) **PCT No.: PCT/EP01/12147**(30) **Foreign Application Priority Data**

Oct. 21, 2000 (DE)..... 10052242.4

Publication Classification(51) **Int. Cl.⁷ H01M 8/10; H01M 10/40;
C08J 5/22**(52) **U.S. Cl. 429/33; 429/314; 521/27**(57) **ABSTRACT**

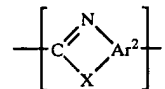
The invention relates to an acid-doped, single-layer or multilayer polymer membrane comprising at least one layer A of a polymer blend comprising

- a) from 0.1 to 99.9% by weight of one or more polymers comprising recurring azole units of the formula 1A and/or 1B:



(1A)

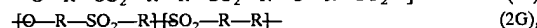
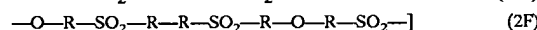
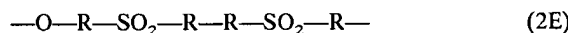
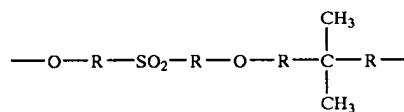
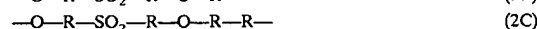
-continued



(1B)

where the radicals Ar, Ar¹ and Ar² are tetravalent, divalent or trivalent aromatic or heteroaromatic groups and the radicals X, which are identical within a repeating unit, are each an oxygen atom, a sulfur atom or an amino group bearing a hydrogen atom, a group having 1-20 carbon atoms, preferably a branched or unbranched alkyl or alkoxy group, or an aryl group as further radical, in admixture with

- b) from 99.9 to 0.1% by weight of a polysulfone comprising recurring units of the formula 2A, 2B, 2C, 2D, 2E, 2F and/or 2G and having no sulfonic acid groups:



where the radicals R are identical or different and are each, independently of one another, 1,2-phenylene, 1,3-phenylene, 1,4-phenylene, 4,4'-biphenyl, a divalent radical of a heteroaromatic, a divalent radical of a C₁₀-aromatic and/or a divalent radical of a C₁₄-aromatic.

Furthermore, a process for producing the doped polymer membrane, its use in fuel cells, in electrolysis, in capacitors, in battery systems and in electrochromic applications and also membrane electrode units comprising at least one polymer membrane according to the invention are described.

EXHIBIT

tabbiter

A

NOVEL MEMBRANES HAVING IMPROVED MECHANICAL PROPERTIES, FOR USE IN FUEL CELLS

[0001] Acid-doped, single-layer or multilayer polymer membrane having layers comprising polymer blends comprising polymers having recurring azole units, process for producing such polymer membranes and their use.

[0002] The present invention concerns the field of polymer membranes. In particular, the invention relates to an acid-doped polymer membrane. In addition, the invention relates to a process for preparing the doped polymer membrane and to its use.

[0003] The polymer membrane which has been doped according to the invention can be used in a variety of ways. Owing to its excellent mechanical properties, it is of particular importance as a polymer membrane in fuel cells.

[0004] Polyazole membranes for use in fuel cells are already known. The basic membranes are doped with concentrated phosphoric acid or sulfuric acid and serve as proton conductors in polyelectrolyte membrane fuel cells (PEM fuel cells). Such membranes allow the membrane electrode unit (MEE) to be operated at from 100° C. to 200° C. and in this way significantly increase the tolerance of the catalyst to the carbon monoxide formed as by-product in reforming, so that gas preparation or gas purification is significantly simplified.

[0005] Disadvantages of these membranes are their mechanical instability with a low E modulus, a low tear strength and a low upper flow limit and also their relatively high permeability to hydrogen and oxygen.

[0006] Kerres, J. et al. (Kerres, Jochen; Ullrich, Andreas; Meier, Frank; Häring, Thomas "Synthesis and characterization of novel-acid-base polymer blends for application in membrane fuel cells" Solid State Ionics 125, 243 to 249, 1999) provide membranes of sulfonated polyether ether ketone sPEEK @Victrex or polyether sulfone sPSU @Udel and PSU @Udel which has been diaminated in the ortho position relative to the sulfone bridge, poly(4-vinylpyridine), poly(benzimidazole) PBI @Celazole or poly(ethylenimine) PEI. These membranes display good proton conductivity at an ion exchange capacity IEC of 1 (IEC=meq of SO₃H/g of dry membrane) and a good thermal stability.

[0007] However, they have the disadvantage that the conductivity of the membranes breaks down under atmospheric pressure above 100° C. due to the loss of water. For this reason, these membranes cannot be used in fuel cells above 100° C. under atmospheric pressure.

[0008] In view of the prior art, it is an object of the present invention to provide a doped polymer membrane having improved properties. The polymer membrane of the invention should display good proton conductivities and a low permeability to hydrogen and oxygen.

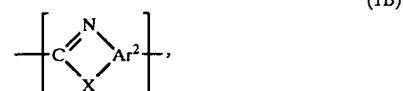
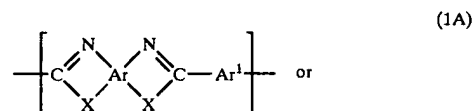
[0009] A further object is to provide a doped polymer membrane which can be used in fuel cells. In particular, the doped polymer membrane should be suitable for use in fuel cells above 100° C. under atmospheric pressure.

[0010] It is also an object of the invention to provide a process for producing the doped polymer membrane, which process can be carried out in a simple way, inexpensively and on an industrial scale.

[0011] These and further objects which have not been explicitly mentioned but can be readily derived or concluded from the relationships discussed briefly here are achieved by an acid-doped polymer membrane having all the features of claim 1. Advantageous embodiments of the doped polymer membrane of the invention are claimed in the subordinate claims which refer back to claim 1. A process for producing the doped polymer membrane of the invention is described in the process claim, while the claims in the use category claim preferred uses of a polymer membrane which has been doped according to the invention.

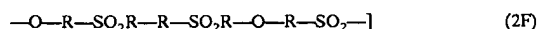
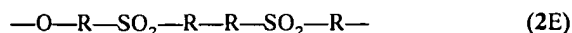
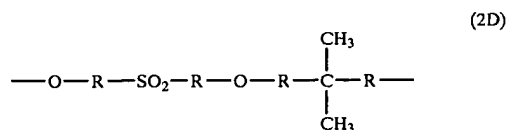
[0012] Provision of an acid-doped, single-layer or multilayer polymer membrane comprising at least one layer A of a polymer blend comprising

[0013] a) from 0.1 to 99.9% by weight of one or more polymers comprising recurring azole units of the formula 1A and/or 1B:



[0014] where the radicals Ar, Ar¹ and Ar² are tetravalent, divalent or trivalent aromatic or heteroaromatic groups and the radicals X, which are identical within a repeating unit, are each an oxygen atom, a sulfur atom or an amino group bearing a hydrogen atom, a group having 1-20 carbon atoms, preferably a branched or unbranched alkyl or alkoxy group, or an aryl group as further radical, in admixture with

[0015] b) from 99.9 to 0.1% by weight of a polysulfone comprising recurring units of the formula 2A, 2B, 2C, 2D, 2E, 2F and/or 2G and having no sulfonic acid groups:



[0016] where the radicals R are identical or different and are each, independently of one another, 1,2-phenylene, 1,3-phenylene, 1,4-phenylene, 4,4'-biphenyl, a divalent radical of a heteroaromatic, a divalent radical of a C₁₀-aromatic and/or a divalent radical of a C₁₄-aromatic,

[0017] makes it possible, in a manner which could not readily have been foreseen, to obtain a doped polymer membrane having improved mechanical properties, in particular an increased E modulus and improved fracture strength.

[0018] At the same time, the doped polymer membranes of the invention display a series of further advantages. These include, inter alia:

[0019] \Rightarrow The doped polymer membranes display good proton conductivities.

[0020] \Rightarrow The doped polymer membranes have only a low permeability to hydrogen and oxygen.

[0021] \Rightarrow Even extremely thin, doped polymer membranes having a total thickness in the range from 10 to 100 μm have sufficiently good material properties at 100° C., in particular a very high mechanical stability and a low permeability to hydrogen and oxygen.

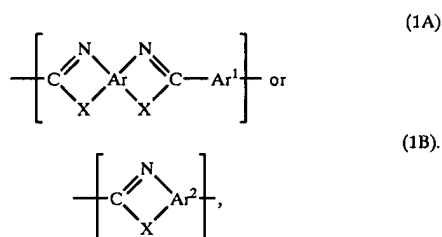
[0022] \Rightarrow The property profile of the doped polymer membrane can be improved further by means of a multilayer structure.

[0023] \Rightarrow The doped polymer membrane is suitable for use in fuel cells above 100° C., in particular under atmospheric pressure.

[0024] \Rightarrow Partial replacement of the comparatively expensive polyazole by comparatively cheap polysulfone provides a doped polymer membrane which is cheaper to produce.

[0025] \Rightarrow The doped polymer membrane can be produced in a simple way and on an industrial scale.

[0026] According to the present invention, the polymer membrane comprises at least one layer A of a polymer blend which comprises from 0.1 to 99.9% by weight of one or more polymers comprising recurring azole units of the formula 1A and/or 1B:



[0027] The radicals Ar, Ar¹ and Ar² are tetravalent, divalent or trivalent aromatic or heteroaromatic groups which may each have one or more rings. Preferred groups are derived from benzene, naphthalene, biphenyl, diphenyl ether, diphenylmethane, diphenyldimethylmethane, bisphenone, diphenyl sulfone, quinoline, pyridine, anthracene and phenanthrene, which may also be substituted. Ar¹ can have any substitution pattern; in the case of phenylene, Ar¹ can be, for example, ortho-, meta- or para-phenylene. Particularly preferred groups are derived from benzene and biphenyl which may also be substituted.

[0028] The radicals X are each an oxygen atom (benzoxazole unit), a sulfur atom (benzothiazole unit) or an amino group (benzimidazole unit) bearing a hydrogen atom, a

group having 1-20 carbon atoms, preferably a branched or unbranched alkyl or alkoxy group, or an aryl group as further radical. Preferred alkyl groups are short-chain alkyl groups having from 1 to 4 carbon atoms, e.g. methyl, ethyl, n- or i-propyl and t-butyl groups. Preferred aromatic groups are phenyl or naphthyl groups. The alkyl groups and the aromatic groups may be substituted. Preferred substituents are halogen atoms such as fluorine, amino groups or short-chain alkyl groups such as methyl or ethyl groups.

[0029] If polyazoles comprising recurring units of the formula (1A) are used for the purpose of the present invention, the radicals X should be identical within a recurring unit.

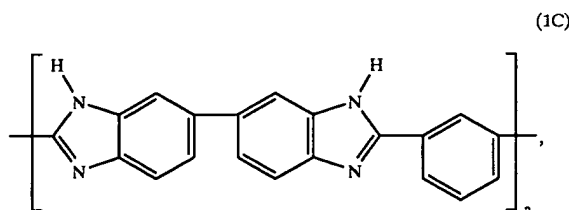
[0030] A polyazole used for the purposes of the invention can in principle comprise different recurring units which, for example, differ in their radical X. However, it preferably has only identical recurring units.

[0031] In a preferred embodiment of the present invention, the polymer comprising recurring azole units is a copolymer comprising at least two units of the formula (1A) and/or (1B) which differ from one another.

[0032] In a particularly preferred embodiment of the present invention, the polymer comprising recurring azole units is a polyazole consisting of only units of the formula (1A) and/or (1B).

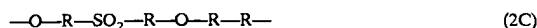
[0033] The number of recurring azole units in the polymer is preferably greater than or equal to 10. Particularly preferred polymers contain at least 100 recurring azole units.

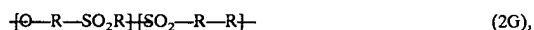
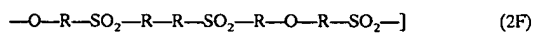
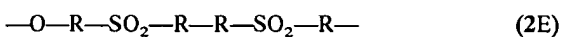
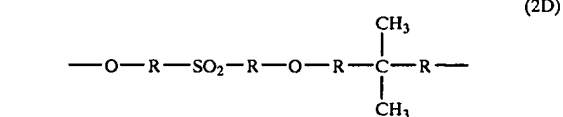
[0034] For the purposes of the present invention, preference is given to using polymers comprising recurring benzimidazole units. An example of an extremely advantageous polymer comprising recurring benzimidazole units is represented by the formula (1C):



[0035] where n is an integer greater than or equal to 10, preferably greater than or equal to 100.

[0036] According to the present invention, the polymer blend comprises from 99.9 to 0.1% by weight of a polysulfone which contains no sulfonic acid groups. The polysulfone comprises recurring units having linking sulfone groups corresponding to the formulae 2A, 2B, 2C, 2D, 2E, 2F and/or 2G:

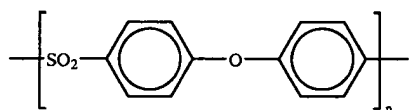




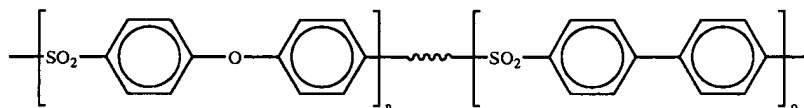
[0037] where the radicals R are identical or different and are each, independently of one another, 1,2-phenylene, 1,3-phenylene, 1,4-phenylene, 4,4'-biphenyl, a divalent radical of a heteroaromatic, a divalent radical of a C₁₀-aromatic and/or a divalent radical of a C₁₄-aromatic. Examples of heteroaromatics are pyridine and quinoline. An example of a C₁₀-aromatic is naphthalene, and an example of a C₁₄-aromatic is phenanthrene.

[0038] Polysulfones which are preferred for the purposes of the present invention include homopolymers and copolymers, for example random copolymers such as @Victrex 720 P and @Astrel. Particularly preferred polysulfones are:

@Victrex 200 P

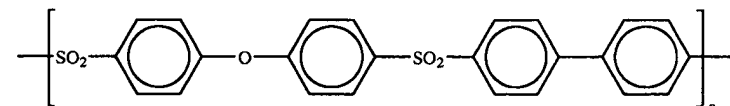


@Victrex 720 P

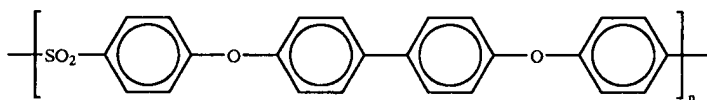


where $n > 0$

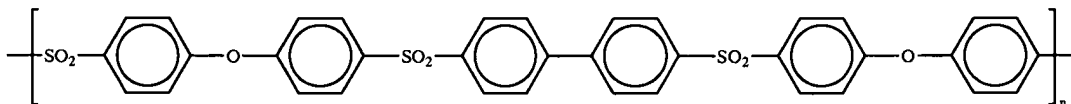
@Radel



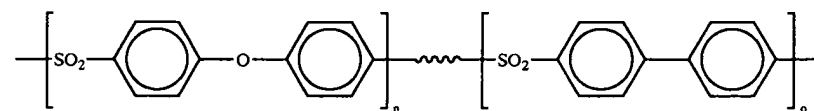
@Radel R



@Victrex HTA

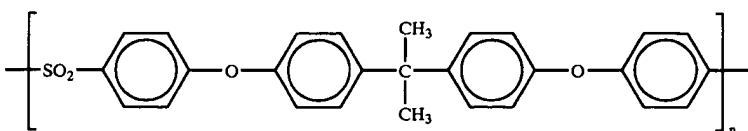


@Astrel



where $n < o$

@Udel



(2H)

(2I)

(2J)

(2K)

(2L)

(2M)

(2N)

[0039] A very particularly preferred polysulfone is ©Radel R.

[0040] The polysulfones which can be used according to the invention may, if desired, be substituted. However, they must contain neither protonated sulfonic acid groups



[0041] nor protonatable sulfonic acid salt groups



[0042] where M^+ is an inorganic or organic cation, because these can impair the mechanical properties of the doped polymer membrane.

[0043] In a preferred embodiment of the present invention, the polysulfones are unsubstituted.

[0044] In another preferred embodiment of the present invention, the number average molecular weight of the polysulfones is greater than 30 000 g/mol.

[0045] The polymer membranes of the invention are doped. For the purposes of the present invention, doped polymer membranes are polymer membranes which due to the presence of dopants display an increased proton conductivity compared to the undoped polymer membranes. Dopants for the polymer membranes of the invention are acids. In this context, acids include all known Lewis and Brønsted acids, preferably inorganic Lewis and Brønsted acids. Furthermore, the use of polyacids, in particular isopolyacids and heteropolyacids and of mixtures of various acids is also possible. For the purposes of the present invention, heteropolyacids are inorganic polyacids having at least two different central atoms which are formed from weak, polybasic oxo acids of a metal (preferably Cr, Mo, V, W) and of a nonmetal (preferably As, I, P, Se, Si, Te) as partial mixed anhydrides. They include, inter alia, 12-molybdophosphoric acid and 12-tungstophosphoric acid.

[0046] Particularly preferred dopants according to the invention are sulfuric acid and phosphoric acid. A very particularly preferred dopant is phosphoric acid (H_3PO_4).

[0047] The degree of doping can be used to influence the conductivity of the polymer membrane of the invention. The conductivity increases with increasing concentration of the dopant until a maximum value is reached. According to the invention, the degree of doping is reported as mol of acid per mole of repeating unit of the polymer. For the purposes of the present invention, a degree of doping of from 3 to 15, in particular from 6 to 12, is preferred.

[0048] The property spectrum of the polymer membrane of the invention can be altered by varying its composition. In a preferred embodiment of the present invention, the polymer blend comprises

[0049] a) from 50 to 99% by weight of a polymer comprising recurring azole units of the formula 1A and/or 1B,

[0050] in admixture with

[0051] b) from 1 to 50% by weight of a polysulfone which has no sulfonic acid groups.

[0052] In a particularly preferred embodiment of the present invention, the polymer blend comprises

[0053] a) from 70 to 95% by weight of a polymer comprising recurring azole units of the formula 1A and/or 1B,

[0054] in admixture with

[0055] b) from 5 to 30% by weight of a polysulfone which has no sulfonic acid groups.

[0056] The doped polymer membrane has a single-layer or multilayer structure. A multilayer structure enables its material properties such as the E modulus, the tensile strength and the proton conductivity to be varied in a desired way. The polymer membrane of the invention preferably comprises at least two layers A and B which are each obtainable from the polymer blend according to the invention and differ from one another in the content of polysulfone b). In addition, it is particularly advantageous for the thicknesses of the two layers A and B also to be different.

[0057] According to the invention, particular preference is given to a doped polymer membrane which comprises at least three layers A, B and C which are each obtainable from the polymer blend according to the invention, with the middle layer C differing from the two outer layers A and B in the content of polysulfone b). Variation of the layer thicknesses can likewise be advantageous. In a particularly preferred embodiment of the present invention, the doped polymer membrane comprises three layers A, B and C. Here, the outer layers A and B are thinner than the middle layer C and have a higher content of polysulfone b) than the middle layer C. In a very particularly preferred embodiment of the present invention, the middle layer C contains no polysulfone.

[0058] The properties of the polymer membrane of the invention can be controlled to some extent by its total thickness. However, even extremely thin polymer membranes have very good mechanical properties and a low permeability to water and oxygen. They are therefore suitable for use in fuel cells at above 100° C., in particular for use in fuel cells at above 120° C., without the edge region of the membrane electrode unit having to be reinforced. The total thickness of the doped polymer membrane of the invention is preferably in the range from 5 to 100 μm , advantageously from 10 to 90 μm , in particular from 20 to 80 μm .

[0059] The polymer membrane of the invention has improved material properties compared to the previously known doped polymer membranes. In particular, it has very good mechanical properties and a low permeability to hydrogen and oxygen. In a particularly preferred embodiment of the present invention, its proton conductivity at room temperature is above 30 mS/cm and its E modulus after 10 minutes at 100° C. is greater than 10 MPa.

[0060] Processes for preparing doped polymer membranes are known. In a preferred embodiment of the present invention, they are obtained by wetting a polymer blend according to the invention with concentrated acid, preferably highly concentrated phosphoric acid, for an appropriate time, preferably 0.5-96 hours, particularly preferably 1-72 hours, at temperatures in the range from room temperature to 100° C. and atmospheric or superatmospheric pressure.

[0061] For the purposes of the present invention, "polymer blends" are physical mixtures of polymers. Processes for

preparing polymer blends are known. They can be obtained, for example, from a solution containing the polymers to be blended by evaporation of the solvent. The evaporation of the solvent is preferably carried out in such a way that a self-supporting and preferably transparent film is obtained. For the purposes of the present invention, N,N-dimethylacetamide, N,N-dimethylformamide, dimethyl sulfoxide, N-methylpyrrolidone or mixtures of these solvents are preferably used.

[0062] Possible applications of the doped polymer membranes of the invention include, inter alia, the use in fuel cells, in electrolysis, in capacitors and in battery systems. Owing to their property profile, the doped polymer membranes are preferably used in fuel cells.

[0063] The present invention also provides a membrane electrode unit which comprises at least one polymer membrane according to the invention. For further information on membrane electrode units, reference may be made to the technical literature, in particular the patents U.S. Pat. No. 4,191,618, U.S. Pat. No. 4,212,714 and U.S. Pat. No. 4,333,805, whose disclosure is hereby explicitly incorporated by reference into the present patent application.

[0064] The invention is illustrated below by means of examples and comparative examples, without the invention being restricted to these examples.

1. EXAMPLE

[0065] a) Preparation of a PBI-DMAc Solution

[0066] @Celazole from Celanese is dissolved in N,N-dimethylacetamide (15% by weight of Celazole) at a temperature of 200° C. over a period of 2-4 hours.

[0067] b) Preparation of a Polysulfone Solution

[0068] Polysulfone @Radel-R 5700 from Amoco (or polyether sulfone @Ultrason E 6000 from BASF) is dissolved in N,N-dimethylacetamide or N-methylpyrrolidone (15% by weight). The polysulfone solution is filtered through a pressure filter at room temperature.

[0069] c) Preparation of the Polymer Mixture in Solution

[0070] The PBI-DMAc solution and the polysulfone solution are mixed by means of a slow-running anchor stirrer at a temperature of 60-95° C. Lower temperatures or high rotational speeds of the stirrer lead, as a result of the Weissenberg effect which is displayed by the polybenzimidazole solution, to at least partial demixing of the solution. The mixed solution is degassed by application of a vacuum for a period of at least 15 minutes at a temperature of 80° C.

[0071] d) Production of the Polymer Membrane

[0072] The solution is applied in a thickness of about 250 μm by means of a doctor blade to a glass plate in a low-dust environment (laminar flow box) and dried at temperatures of up to 120° C. in a convection drying oven provided with a dust filter. The dried polymer membrane is peeled off from the glass plate.

[0073] e) Doping of the Polymer Membrane

[0074] The membrane is wetted with 85% strength phosphoric acid for 72 hours at room temperature.

2. COMPARATIVE EXAMPLE

[0075] Victrex polyether ketone (PEK) is, as described in DE 19847782 A1 20000420, converted into the sulfonated product. The sulfonated product has a degree of sulfonation of 42%. The sulfonic acid polymer is converted into the sodium salt by stirring overnight in 5% strength aqueous sodium hydroxide at 50° C., filtered off, washed and dried.

[0076] The sulfonic acid polymer is dissolved in N,N-dimethylacetamide or N-methylpyrrolidone (15% by weight). The polysulfone solution is filtered through a pressure filter at room temperature.

[0077] The dissolution of the polymer is carried out in a manner analogous to 1.b). Conversion of the sodium salt into the free acid is carried out by treatment of the blend membrane with phosphoric acid. The preparation of the polymer mixture in solution, the production of the polymer membrane and the doping of the membrane are carried out by methods analogous to those in the above example.

[0078] 3. Determination of the Phosphoric Acid Concentration

[0079] The doped membranes are stirred overnight in precisely 1 l of distilled water. They are then taken from the water and dried at 150° C. and 20-50 mbar for 3 hours. The dried membranes are weighed. The acid content of the water is determined by titration with a standard solution of sodium hydroxide.

[0080] The number of acid molecules per repeating unit of the respective polymer is calculated from the dry mass of the membrane and the titration data. The results obtained are summarized in table 1.

TABLE 1

Degree of doping of the polymer membrane		
Sample	Blending component [%]	H ₃ PO ₄ /repeating unit of the polymer
E 1	5% PES	9.26
E 2	10% PES	8.75
E 3	20% PES	8.44
E 4	5% PSU	9.29
E 5	10% PSU	8.92
E 6	20% PSU	7.75
CE 1	0%	9.35
CE 2	5% sPEK	9.85
CE 3	10% sPEK	9.51
CE 4	20% sPEK	8.76

E: Example;

CE: Comparative example

[0081] 4. Measurement of the Conductivity

[0082] Measurements were carried out at room temperature by means of a 4-pole arrangement using platinum electrodes (wire, 0.25 mm diameter) and a Zahner IM 6 impedance spectrometer. The spectrum obtained is fitted using a simple model consisting of a parallel circuit, a capacitor and a resistance. The dimensions of the sample were determined prior to doping. The results are shown in table 2.

TABLE 2

Conductivity measurements										
Sample	Blending component	Fitting results				Membrane				
		R [ohm]	Error [%]	C _{par} [pF]	Error [%]	Thickness [cm]	Error [%]	Width [cm]	Error [%]	Conductivity [S/cm]
E 1	5% PES	2004	2.67	102.2	23.16	3.2E-03	1.0	3.5	3.0	0.0891
E 2	10% PES	2293	2.45	119.7	17.39	3.1E-03	1.0	3.5	3.0	0.0804
E 3	20% PES	2756	3.21	131.4	23.31	2.8E-03	1.0	3.5	3.0	0.074
E 4	5% PSU	2395	1.58	120.5	18.21	3.3E-03	1.0	3.5	3.0	0.072
E 5	10% PSU	2392	2.77	127.9	10.64	3.3E-03	1.0	3.5	3.0	0.072
E 6	20% PSU	2923	2.06	126.5	18.40	3.0E-03	1.0	3.5	3.0	0.065
CE 1	0	2091	2.72	115.9	27.52	2.9E-03	1.0	3.5	3.0	0.094
CE 2	05% sPEK	2485	1.29	122.8	20.37	2.9E-03	1.0	3.5	3.0	0.079
CE 3	10% sPEK	2797	0.72	123.0	15.90	2.7E-03	1.0	3.5	3.0	0.076
CE 4	20% sPEK	3191	2.64	129.1	16.21	3.2E-03	1.0	3.5	3.0	0.056

E: Example;

CE: Comparative example

PSU (Radel R5700);

PES (Ultrason E6000);

PEK [M420 (Op. 3/99) Na salt]

[0083] 5. Measurement of the Mechanical Properties

[0084] The mechanical properties are determined in a uniaxially tensile test on a Zwick testing machine (100 N load cell). The geometry of the test specimen is determined in the undoped state. The specimen width in the undoped state is 15 mm, and the specimen length between the pneumatically operated chucks is 100 mm.

[0085] The initial force is 0.1 N, and the test is carried out at a speed of 100 mm/min.

[0086] The samples are installed in the sample chamber preheated to 100° C., the sample chamber is closed and the measurement is started after precisely 10 minutes. Table 3 summarizes the results.

TABLE 3

Measurement of the mechanical properties				
Sample	E modulus [MPa]	Fracture toughness [J/m ²]	Elongation at F _{max} [%]	R _{max} [N/mm ²]
E 1	8.67	37733	24.41	1.75
E 2	8.32	32590	27.80	1.67
E 3	8.04	47931	33.14	1.99
E 4	7.21	41715	27.25	1.60
E 5	9.81	22473	20.22	1.62
E 6	22.59	190428	55.90	4.66
E 1	7.71	23263	22.06	1.51
CE 2	8.27	47650	33.08	1.97
E 3	7.52	37561	27.87	1.93
CE 4	6.65	47483	38.68	1.72

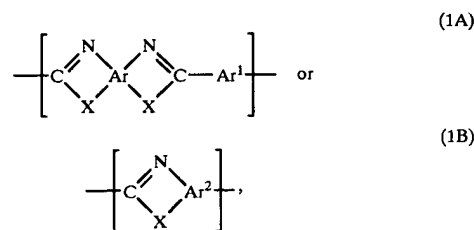
E: Example;

CE: Comparative example

F_{max}: Maximum force in the tensile stress/elongation curveR_{max}: Ultimate tensile strength

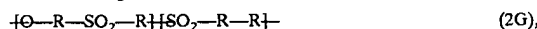
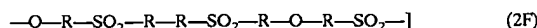
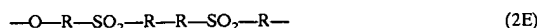
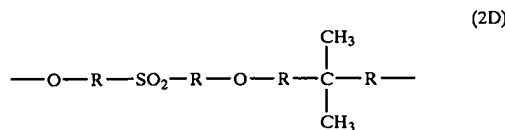
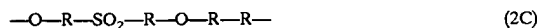
1. An acid-doped, single-layer or multilayer polymer membrane comprising at least one layer A of a polymer blend comprising

- a) from 0.1 to 99.9% by weight of one or more polymers comprising recurring azole units of the formula 1A and/or 1B:



where the radicals Ar, Ar¹ and Ar² are tetravalent, divalent or trivalent aromatic or heteroaromatic groups and the radicals X, which are identical within a repeating unit, are each an oxygen atom, a sulfur atom or an amino group bearing a hydrogen atom, a group having 1-20 carbon atoms, preferably a branched or unbranched alkyl or alkoxy group, or an aryl group as further radical, in admixture with

- b) from 99.9 to 0.1% by weight of a polysulfone comprising recurring units of the formula 2A, 2B, 2C, 2D, 2E, 2F and/or 2G and having no sulfonic acid groups:

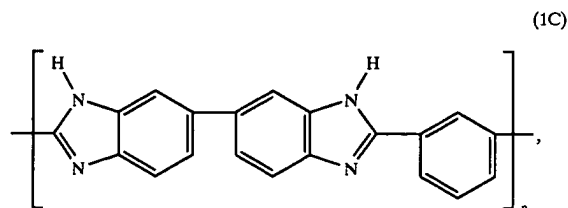


where the radicals R are identical or different and are each, independently of one another, 1,2-phenylene,

1,3-phenylene, 1,4-phenylene, 4,4'-biphenyl, a divalent radical of a heteroaromatic, a divalent radical of a C₁₀-aromatic or a divalent radical of a C₁₄-aromatic.

2. A doped polymer membrane as claimed in claim 1, wherein the number of recurring azole units in the polymer is greater than or equal to 10, in particular greater than 100.

3. A doped polymer membrane as claimed in either of the preceding claims, wherein the polymer a) is a polymer comprising recurring benzimidazole units of the formula 1C):



where n is an integer greater than or equal to 10.

4. A doped polymer membrane as claimed in any of the preceding claims, wherein the polysulfone is of the type @Victrex 200 P, @Victrex 720 P, @Radel, @Radel R, @Victrex HTA, @Astrel oer @Udel.

5. A doped polymer membrane as claimed in one or more of the preceding claims, wherein the polysulfone is of the type @Radel R.

6. A doped polymer membrane as claimed in one or more of the preceding claims, which is doped with an inorganic Lewis or Brønsted acid, preferably with hydrochloric acid, sulfuric acid and/or phosphoric acid.

7. A doped polymer membrane as claimed in one or more of the preceding claims, wherein the polymer blend comprises

a) from 50 to 99% by weight of a polymer comprising recurring azole units of the formula 1A and/or 1B,

in admixture with

b) from 1 to 50% by weight of a polysulfone comprising recurring units of the formula 2A, 2B, 2C, 2D, 2E, 2F and/or 2G which has no sulfonic acid groups.

8. A doped polymer membrane as claimed in one or more of the preceding claims which comprises at least two layers A and B which are each obtainable from a polymer blend as defined in claim 1 and differ from one another in the content of polysulfone b) and preferably in their thickness.

9. A doped polymer membrane as claimed in one or more of claims 1 to 7 which comprises at least three layers A, B and C which are each obtainable from a polymer blend as defined in claim 1, with the middle layer C differing from the two outer layers A and B in the content of polysulfone b).

10. A doped polymer membrane as claimed in claim 9, wherein the middle layer B contains no polysulfone b).

11. A doped polymer membrane as claimed in one or more of the preceding claims which has a total thickness of from 5 to 100 μm .

12. A doped polymer membrane as claimed in one or more of the preceding claims whose proton conductivity at room temperature is above 30 mS/cm and whose E modulus after 10 minutes at 100° C. is greater than 10 MPa.

13. A process for producing a doped polymer membrane as claimed in one or more of the preceding claims, which comprises wetting a polymer blend as defined in the claims with concentrated acid for an appropriate time at temperatures in the range from room temperature to 100° C. and atmospheric or superatmospheric pressure.

14. The use of a doped polymer membrane as claimed in one or more of claims 1 to 12 in fuel cells, in electrolysis, in capacitors or in battery systems.

15. The use as claimed in claim 14 in fuel cells.

16. A membrane electrode unit comprising at least one polymer membrane as claimed in any of claims 1 to 12.

* * * * *